

# Breakdown of scale-invariance in the coarsening of phase-separating binary fluids

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We present evidence, based on lattice Boltzmann simulations, to show that the coarsening of the domains in phase separating binary fluids is not a scale-invariant process. Moreover we emphasise that the pathway by which phase separation occurs depends strongly on the relation between diffusive and hydrodynamic time scales.

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Our aim in this Letter is to discuss domain growth in two-dimensional binary fluid mixtures. When a binary mixture of fluids,  $A$  and  $B$  say, is quenched below its critical point it phase separates into an  $A$ -rich and a  $B$ -rich phase. This is achieved by domains of the two phases forming and then growing. It has been widely assumed that the coarsening of the domains is a scale-invariant process [1]. We present evidence, based on lattice Boltzmann simulations [2], to show that this is not the case for binary fluids where different growth mechanisms compete at all times. We also emphasise that the pathways by which coarsening occurs have a strong qualitative dependence on the relation between diffusive and hydrodynamic time scales.

There is a large body of numerical and experimental data on domain coarsening in systems without hydrodynamics, such as magnets or binary alloys. The conclusion is that, after initial transients, the domain growth is scale invariant. The morphology of the domain pattern remains statistically equivalent at all times apart from a change of the length scale and the correlation function of the order parameter  $\phi$  obeys the scaling form

$$\langle \phi(\mathbf{x} + \mathbf{r}, t) \phi(\mathbf{x}, t) \rangle = f(\mathbf{r}/R(t)) \quad (1)$$

where  $\langle \dots \rangle$  indicates a spatial average and  $R(t)$  is a length scale which is typically observed to grow as a power law

$$R(t) \sim (t - t_0)^\alpha. \quad (2)$$

$\alpha$ , the growth exponent, is a universal constant which is expected to depend only on the growth mechanism and not on the microscopic details of the system.  $t_0$  is a zero time that does not have to coincide with the start of the simulation.

Several different growth mechanisms have been identified or proposed for bicontinuous two-dimensional binary fluids.

**Diffusive growth:** this is the mechanism by which domains grow by the diffusion of material between them [3]. The growth is slow with  $\alpha = 1/3$  as material has to diffuse across a  $B$  domain to move between  $A$  domains and vice versa. This mechanism is common to all materials with a conserved order parameter (e.g. binary alloys,

spin systems with Kawasaki dynamics) and does not rely on the hydrodynamic properties of fluids.

**Diffusion-enhanced collisions:** In a system of concentrated droplets the diffusion field around the droplets leads to an attraction between them [4]. In a fluid they are able to flow in response leading to a faster coalescence, but with  $\alpha$  still  $1/3$ .

**Hydrodynamic growth:** for time scales over which hydrodynamic modes can be excited bulk fluid flow is possible [5]. This is a faster process which leads to a growth exponent  $\alpha = 2/3$  for fluids at long times. However, as we shall demonstrate below, hydrodynamic flow, driven by the pressure difference between points of different curvature, is effective in reducing the interface length and making domains more nearly circular but not in enhancing coalescence of domains.

**Noise-induced growth:** Noise can lead to a growth exponent  $\alpha = 1/2$  [6]. However there is no noise in the lattice Boltzmann results presented here and this mechanism will not be relevant.

In this letter we present evidence that: 1. The competition between diffusive and hydrodynamic growth leads to a breakdown of scale invariance. 2. For very low viscosities capillary waves are important and lead to yet another possible growth mechanism. 3. The relative magnitudes of the diffusion constant, viscosity and surface tension are qualitatively important in determining the route along which domain growth proceeds. In particular we clearly identify the double quench pathway first described by Tanaka [7].

Our evidence for the breakdown of scale invariance in hydrodynamic systems is encapsulated in Figures 1, 2, and 3 which correspond to high, intermediate and low viscosities respectively. The left-hand column of snapshot pictures in each figure shows the domain pattern at three times. Coarsening of the domains can be clearly seen and it is immediately apparent that the shapes of the growing domains depend on the value of the viscosity.

To more easily compare the emerging patterns the right-hand column of snapshots in each of the figures shows an enlargement of part of the corresponding left-hand picture. The enlargement is by a factor  $(t_3/t)^\alpha$  for a picture at time  $t$  where  $t_3$  is the time of the final snap-

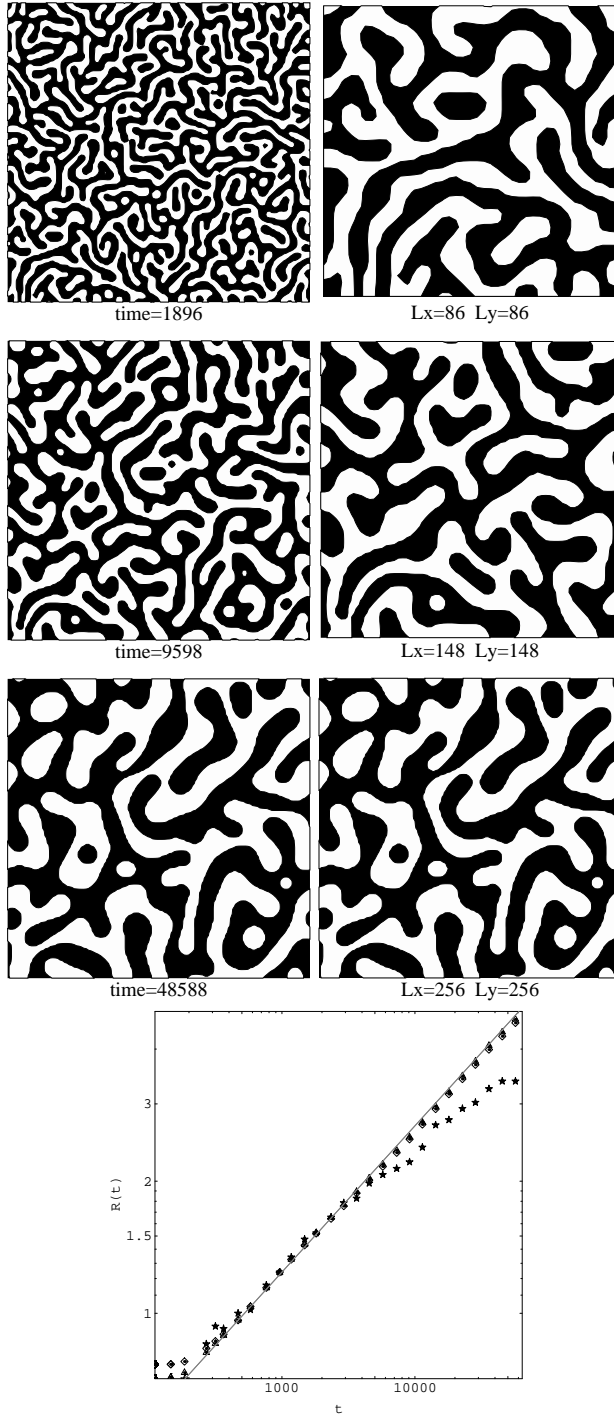


FIG. 1. Evolution of phase-separating domains for a binary fluid with high viscosity. The left-hand column shows the phase ordering process at three different times. The right-hand column shows each snapshot scaled by a factor  $(t/48588)^{1/3}$ . The resulting box size  $(L_x, L_y)$  is indicated. The graph at the base of the figure shows the behaviour of  $\ln R$  as a function of  $\ln t$  where  $R$  is a length scale and  $t$  the time. Different scales are distinguished by  $\diamond(R^1)$ ,  $\triangle(R^o)$ , and  $\ast(R^\#)$ . The line corresponds to  $\alpha = 1/3$ .

shot and  $\alpha^1$  is the growth exponent for the length scale

$R^1$  defined below. If the system is scale invariant all the figures in the right-hand column would be expected to look (statistically) identical.

To obtain a more quantitative measure of the growth a graph of  $\ln R(t)$  as a function of  $\ln t$  is also displayed for each value of the viscosity. Three different measures of length are considered. Previous work [8] has concentrated on measuring  $R^1(t)$ , the inverse first moment of the circularly averaged structure factor. Here we also present results for length scales derived from the length of the interface  $L_I$  and the number of domains  $N$

$$R^o(t) = \frac{L_x \ast L_y}{L_I}, \quad R^\#(t) = \sqrt{\frac{L_x L_y}{N}} \quad (3)$$

respectively where  $L_x$  and  $L_y$  are the linear dimensions of the simulation box.

If the system is scale invariant all lengths should scale with the same value of  $\alpha$ . (This excludes microscopic lengths, such as the lattice spacing and interface widths, which remain unchanged during the growth process.) We show that the different lengths do not scale in the same way for some values of the fluid viscosity. This implies a breakdown of scale invariance which is further supported by visual inspection of the growing domains.

We consider each value of the viscosity in turn. At very high viscosities (Figure 1) hydrodynamics is unimportant. Therefore the system resembles Model B (growth with a conserved order parameter) in the language of critical phenomena. Diffusive growth, with  $\alpha = 1/3$ , is expected. The length scales  $R^1$  and  $R^o$  clearly show this behaviour. For early times  $R^\#$  also scales as  $t^{1/3}$  but there is a slower growth for later times. This was a feature of all the simulations we ran and became more pronounced for the larger systems. A possible explanation lies in the lack of a bicontinuous structure in two dimensions which leads to the formation of nested structures which affect the growth. The snapshots on the right-hand side of Figure 1 show no visual evidence for a breakdown of scaling.

Figure 2 shows results for intermediate viscosities which are low enough to allow hydrodynamic flow but sufficiently high to damp out capillary waves. The well-known hydrodynamic growth exponent  $2/3$  is observed for  $R^1$  and  $R^o$  but for  $R^\#$  the growth exponent quickly crosses over to  $\alpha^\# = 1/3$ . This implies that the number of domains is decreasing more slowly than in a scale-invariant state. It occurs because, although the interface curvature of the domains is rapidly decreased by the flow, once the domains are circular hydrodynamics can only assist the growth through the much slower diffusion-enhanced collisions which proceed with  $\alpha = 1/3$  [4].

As a result domains on large length scales are tortuous. The smaller the domains the more circular they become. The length scale of the crossover between these behaviours increases with time. Hence as time progresses an increasingly deep hierarchy of circular domains within

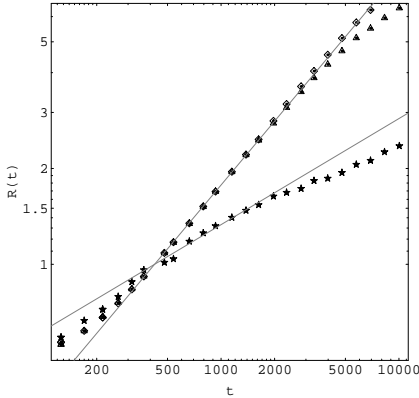
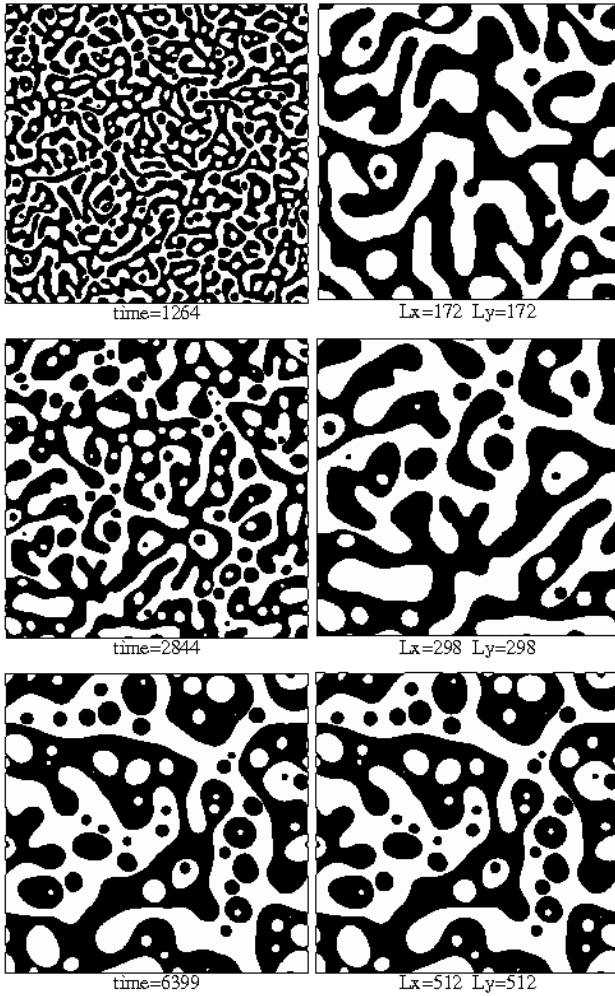


FIG. 2. As Figure 1 but for an intermediate value of the viscosity. Scaling is by a factor  $(t/6399)^{2/3}$ . The lines correspond to  $\alpha = 2/3$  and  $1/3$ .

circular domains results. Pictorial evidence for the lack of scale invariance in the growth process can be seen in the scaled snapshots in Figure 2.

In most simulations of hydrodynamic growth results have been limited to  $R^1$  (but see [9] where several different measures are used for a one-component fluid). This gives most weight to the largest domains which continue

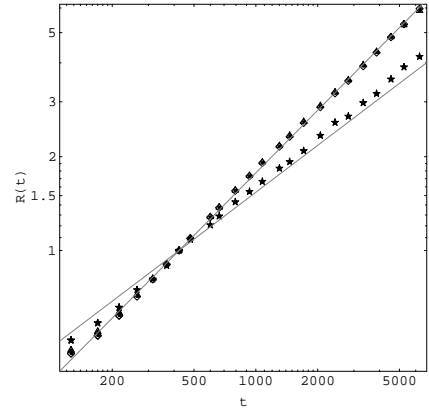
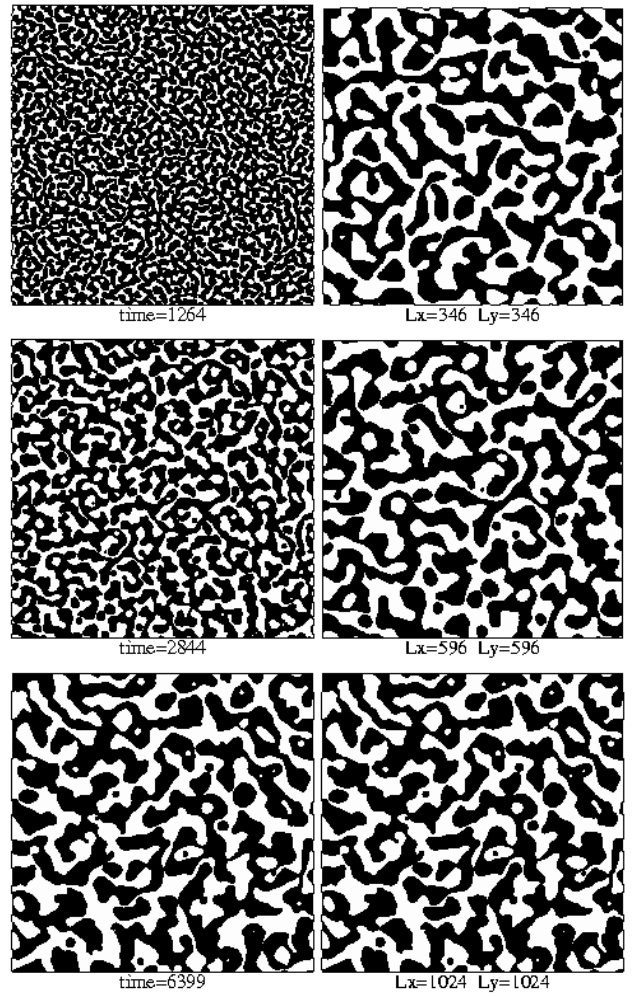


FIG. 3. As Figure 1 but for a low value of the viscosity. Scaling is by a factor  $(t/6399)^{2/3}$ . The lines correspond to  $\alpha = 2/3$  and  $1/2$ .

to grow via the  $2/3$  power law and this is the exponent that has been widely reported [8]. The measure  $R^\circ$  is derived from the interface length. Initially this is mostly in the larger domains and  $R^\circ$  is not sensitive to the structural change. For late times there is some indication that the growth of this measure is slowing down.  $R^\#$  however is related to the number of domains and provides a good

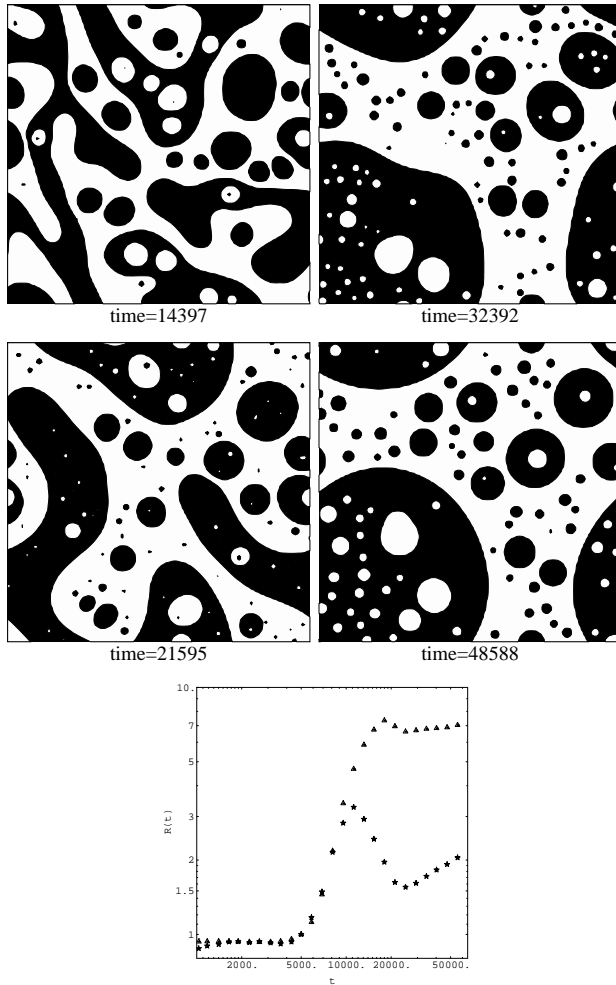


FIG. 4. The evolution with time of phase separating domains for a binary fluid with intermediate viscosity but low diffusivity. Domains quickly become circular but the order parameter does not reach its equilibrium value. Hence a second crop of domains forms by spinodal decomposition. Tanaka has termed this a double quench.  $R(t)$  shows no clear scaling behaviour (see Figure 1 caption for definition of symbols).

measure of the smaller scale features of the pattern.

At low viscosities (Figure 3) the morphology of the domain growth is again altered. Now the damping of capillary waves is so small that their amplitude can be of order of the domain size. The real-space pictures of the growth show rugged interfaces. This enhances the domain coalescence and the growth law for  $R^\#$  is changed from  $1/3$  to  $1/2$ .

Finally in Figure 4 we show yet another pathway to phase separation in a binary fluid, the double quench first described by Tanaka [7]. These results were obtained for intermediate viscosities but a low value of the diffusion coefficient. Domains are created and hydrodynamic flow allows them to attain a circular shape. However, because of the weak diffusivity this occurs before the order parameter in each domain attains its equilibrium value. Hence secondary spinodal decomposition can take place within

each domain and a nested hierarchy of circular domains form up to a length scale which increases with time. Plots of the the logarithm of the length scales against the logarithm of time in Figure 4 show no clear scaling behaviour on length and time scales accessible to the simulations.

These results were obtained using the lattice Boltzmann approach described in [2]. This gives a numerical solution of the continuity, Navier-Stokes and convection-diffusion equations describing the flow of binary fluids. There are two particularly relevant advantages of the method. Firstly it is possible to vary the diffusivity and the viscosity over a wide range. Secondly the equilibrium state minimises an input free energy which here is taken to be that of a model binary fluid.

To conclude, domain growth in binary fluids is a richer phenomenon than hitherto described. The dominant growth mechanism depends strongly on the viscosity and diffusivity of the fluid and may be different at different length and time scales. Many questions remain, among them clarification of the growth mechanisms at non-symmetric compositions, investigation of the rôle of noise, clarification of the importance of self-diffusion in liquid-gas systems and assessment of the effect of anisotropy in the dynamics of the two phases.

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